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## DISCLAIMER

## ABTRACT

The University/National Energy Technology Laboratory (NETL) Student Partnership Program stimulated basic and applied research in Energy and Environmental Science areas through NETL's Office of Science and Technology (OST). This Partnership Program supported the education of graduate students in Energy and Environmental Sciences, while fostering increased scientific interaction between NETL and the participating universities, by providing graduate student support for research at a NETL facility under the joint supervision of NETL and university faculty. Projects were intended to enhance a previously established scientific or engineering relationship or to create a new relationship. Major areas of research under the Partnership Program included $CO_2$ sequestration, granular solids flow, multi-phase flow in porous solids, gas hydrates, nanotubes, acid-mine flow identification and remediation, water-gas shift reaction, circulating fluidized beds, slurry bubble column, fuel desulphurization, carbon fibers, and fuel cells.

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## EXECUTIVE SUMMARY

Effective Faculty/NETL Mentor/Graduate Student relationships were developed through the University/NETL Student Partnership Program process and, due to the support by this program, at least 17 Ph.D. dissertations and 7 MS theses resulted which under this contract were acceptable in lieu of a technical report. The dissertation/theses titles, authors and NETL mentors for work supported under the Program include the following:

1. "$CO_2$ Sorption by Pittsburgh-Seam Coal Subjected to Confining Pressure"
   Michael Hile (S) and Jonathan Mathews (F), The Pennsylvania Sate University,
   with Karl Schroeder (M), NETL.
2. "Optimization of Carbon Dioxide Sequestration Process Design Parameters"
   Fatma Burcu Gorucu (S) and Turgay Ertekin, The Pennsylvania Sate University,
   with Duane Smith (M), NETL.
3. "Regional Characterization of a Carbon Sequestration Pilot Site with Implications for Enhanced Oil Recovery"
   William Carpenter (S) and Thomas Wilson (F), West Virginia Univeristy, with
   Duane Smith (M) and Arthur Wells (M), NETL.
4. "Fraction Pattern Characterization of the Tensleep Formation, Teapot Dome, Wyoming"
   Bryan Schwartz (S) and Thomas Wilson (F), West Virginia Univeristy, with
   Duane Smith (M), NETL.
5. "Molecular Simulation of Study of Adsorption, Diffusion and Dissociation"
   Liang Chen (S) and Karl Johnson (F), University of Pittsburgh, with
   Kurt Rothenberger (M) and Brad Bockrath (M), NETL.
6. "Phase Equilibrium and Mass Transfer in Hydrate Forming $CO_2$-Water Systems"
   Yi Zhang (S) and Gerald Holder (F), University of Pittsburgh, with
   Robert Warzinski (M), NETL.
7. "Transient and Isotopic Infrared Study of Adsorbed Species on Heterogeneous Catalysts"
   Robert Stevens, Jr. (S), and Steven Chuang (F), University of Akron, with
   Yee Soong (M) and McMahan Gray, NETL.
8. "Fundamentals of Multiphase, Gas-Solid and Gas-Liquid Flows in Porous Media"
   Ali Reza Mazaheri (S) and Goodarz Ahmadi (F), Clarkson University, with
   Duane Smith (M), NETL.
9. "Fundamentals and Applications of Environmental and Geophysical Multiphase Flows"
   Kambiz Nazridoust (S) and Goodarz Ahmadi (F), Clarkson University, with
   Duane Smith (M), NETL.
10. "Simulation of Granular and Gas-Solid Flows using Discrete Element Method"
    Dhanunjay Boyalakuntla (S), Cristina Amon (F), Carnegie Mellon University,
    and Jayathi Murthy, Purdue University, with Thomas O'Brien (M), NETL.
11. "Predicting Gas Separation Membrane Performance from Atomistic Simulations"
    Shong-Shan Chong (S), David Sholl (F), Carnegie Mellon University, with
    Kurt Rothenberger (M), NETL.
12. "Design and Study of Catalytic Activators of Hydrogen Peroxide Promising Rapid, Efficient Petroleum Desulfurization and Bleaching Technologies"
    Yelda Hangun-Balkir (S), Colin Horwitz, and Terrance Collins (F),
    Carnegie Mellon University, with Brett Howard (M), NETL.

13. "First Principles Prediction of Hydrogen Transport in Binary Copper-Palladium Alloy Membranes**"**
Preeti Kamakoti (S) and David Sholl (F), Carnegie Mellon University, with Brad Bockrath (M), NETL.
14. "Simulation of Dense Granular and Fluid-Solid Flow"
Yong Cao (S), Cristina Amon (F), Carnegie Mellon University, and Jayathi Murthy, Purdue University, with Thomas O'Brien (M), NETL.
15. "Design and Understanding of Turbulent, Bubbling and Slurry Bubble Column Reactors"
Jonghwun Jung (S) and Dimitri Gidaspow (F), Illinois Institute of Technology, with Isaac Gamwo (M), NETL.
16. "Characterization of Precipitates Associated with Bituminous Coal Mine Drainage, Northern Appalachian Region, United States"
Candace Kairies (S) and Rosemary Capo (F), University of Pittsburgh, with George Watzlaf (M), NETL.
17. "Evaluation of the Kinetics of Biologically Catalyzed Treatment and Regeneration of Nitrogen Oxide Scrubbing Process Waters**"**
Robert Dilmore (S) and Ronald Neufeld (F), University of Pittsburgh, with Richard Hammack (M), NETL.
18. "The High-Temperature, High-Pressure Homogeneous Water-Gas Shift Reaction in a Membrane Reactor"
Filipe Bustamante (S) and Robert Enick (F), University of Pittsburgh, with Kurt Rothenberger (M) and Bret Howard, NETL.
19. "Environmentally Relevant Adsorption on Carbonaceous Surfaces Studied by Optical Differential Reflectance and Temperature Programmed Desorption"
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20. "Chemistry of the Adsorption of Carbon Dioxide by Argonne Premium Coals and a Model to Simulate Carbon Dioxide Sequestration in Coal Seams"
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23. "Experimental Investigation of Oscillatory Heat Release Mechanisms and Stability Margin Analysis in Lean-Premixed Combustion"
Don Ferguson (S) and Mridul Gautam (F), West Virginia University, with George Richards (M), NETL.
24. "Geophysical Investigation of the T and T Mine Complex, Preston County, West Virginia"
Jennifer Mabie (S) and Thomas Wilson (F), West Virginia University, with Terry Ackman (M), NETL.

The abstracts of these dissertation and theses are included in the appendices of this report.

## I. EXPERIMENTAL

All experimental laboratory work for the Program was conducted at NETL Laboratories. Experimental details for each project may be found within the respective dissertations/theses which are readily available from the respective Universities or on-line thesis/dissertation services such as UMI Microform. Abstracts of each thesis/dissertation are included in the appendices of this report.

## II. RESULTS AND DISCUSSION

Results and discussion for each project may be found within the respective dissertations/theses which are readily available from the respective Universities or on-line thesis/dissertation services such as UMI Microform. Abstracts of each thesis/dissertation are included in the appendices of this report.

## III. CONCLUSIONS

Conclusions for each project may be found within the respective dissertations/theses which are readily available from the respective Universities or on-line thesis/dissertation services such as UMI Microform. Abstracts of each thesis/dissertation are included in the appendices of this report.

## IV. REFERENCES


1. "$CO_2$ Sorption by Pittsburgh-Seam Coal Subjected to Confining Pressure," Hile, Michael Lee, M.S. Thesis, The Pennsylvania Sate University (2006).
2. "Optimization of Carbon Dioxide Sequestration Process Design Parameters," Gorucu, Fatma Burcu, M.S. Thesis, The Pennsylvania Sate University (2005).
3. "Regional Characterization of a Carbon Sequestration Pilot Site with Implications for Enhanced Oil Recovery," Carpenter, William O., Jr., M.S. Thesis, West Virginia University (2005).
4. "Fraction Pattern Characterization of the Tensleep Formation, Teapot Dome, Wyoming," Schwartz, Bryan C., M.S. Thesis, West Virginia University (2006).
5. "Molecular Simulation of Study of Adsorption, Diffusion and Dissociation," Chen, Liang, Ph.D. Dissertation, University of Pittsburgh (2006).
6. "Phase Equilibrium and Mass Transfer in Hydrate Forming $CO_2$-Water Systems" Zhang, Yi, Ph.D. Dissertation, University of Pittsburgh (2007).
7. "Transient and Isotopic Infrared Study of Adsorbed Species on Heterogeneous Catalysts," Stevens, Robert Wayne, Jr., Ph.D. Dissertation, The University of Akron (2003).
8. "Fundamentals of Multiphase, Gas-Solid and Gas-Liquid Flows in Porous Media," Mazaheri, Ali Reza, Ph.D. Dissertation, Clarkson University (2004).
9. "Fundamentals and Applications of Environmental and Geophysical Multiphase Flows," Nazridoust, Kambiz, Ph.D. Dissertation, Clarkson University (2006).

10. “Simulation of Granular and Gas-Solid Flows using Discrete Element Method,” Boyalakuntla, Dhanunjay S., Ph.D. Dissertation, Carnegie Mellon University (2003).
11. “Predicting Gas Separation Membrane Performance from Atomistic Simulations,” Chong, Shang-Shan, Ph.D. Dissertation, Carnegie Mellon University (2005).
12. **“**Design and Study of Catalytic Activators of Hydrogen Peroxide Promising Rapid, Efficient Petroleum Desulfurization and Bleaching Technologies,” Hangun, Yelda, Ph.D. Dissertation, Carnegie Mellon University (2002).
13. “First Principles Prediction of Hydrogen Transport in Binary Copper-Palladium Alloy Membranes,”Kamakoti, Preeti*,* Ph.D. Dissertation, Carnegie Mellon University (2005).
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16. “Characterization of Precipitates Associated with Bituminous Coal Mine Drainage, Northern Appalachian region, United States,” Kairies, Candace Lianne, Ph.D. Dissertation, University of Pittsburgh (2003).
17. **“**Evaluation of the Kinetics of Biologically Catalyzed Treatment and Regeneration of Nitrogen Oxide Scrubbing Process Waters,” Dilmore, Robert Michael, Ph.D. Dissertation, University of Pittsburgh (2004).
18. The High-Temperature, High-Pressure Homogeneous Water-Gas Shift Reaction in a Membrane Reactor,” Bustamante-Londono, Felipe, Ph.D. Dissertation, University of Pittsburgh (2004).
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24. “Geophysical Investigation of the T and T Mine Complex, Preston County, West Virginia,” Mabie, Jennifer S., M.S., West Virginia University (2003).

**Appendices**
**Thesis/Dissertation Abstracts**

## Appendix I.

## Abstract[1]

### "$CO_2$ Sorption by Pittsburgh-Seam Coal Subjected to Confining Pressure"

**Michael Hile, The Pennsylvania Sate University**

Carbon dioxide sequestration by coal will aid in the stabilization of atmospheric $CO_2$ concentrations, thereby reducing the contribution of anthropogenic sources to climate change. Carbon dioxide uptake capacity and sorption kinetics by coal are unrefined in terms of the effect of in-situ conditions of coal seams. LeChatlier.s principle suggests that confining stress will inhibit swelling caused by gas sorption, in turn decreasing sorption capacity itself. Intact, bituminous coal cores from the Pittsburgh #7 seam were dried and evacuated and subjected to unique confining pressures were analyzed for $CO_2$ uptake capacity, sorption kinetics, and strain using a volumetric sorption system with X-ray computed tomography (CT) techniques. As was hypothesized by LeChatlier.s principle above, the apparent $CO_2$ sorption capacity of intact coal samples subjected to confining pressure decreased by as much as 80% compared to the $CO_2$ capacity of powdered coal taken from the same coal core. Carbon dioxide capacity of powdered coal reaches apparent equilibrium in one hour, intact coal cores subjected to confining pressure take weeks reach apparent $CO_2$ sorption equilibrium. An increase from 550 psig to 1,850 psig confining pressure reduces coal matrix swelling during $CO_2$ sorption by 30%. Strain within the coal matrix during $CO_2$ sorption is heterogeneous and anisotropic at a scale of 30 microns and is likely be dependant on microlithotype content. Carbon dioxide uptake capacity was also compared to microlithotypes in three regions of one coal core. Higher transitions in CT number were observed in areas of higher vitrite content. These results implicate confining pressure on dry evacuated cores inhibits the practical $CO_2$ sorption capacity and kinetics.

## Appendix II.

## Abstract[2]

### "Optimization of Carbon Dioxide Sequestration Process Design Parameters"

**Fatma Burcu Gorucu, The Pennsylvania Sate University**

One of the more important environmental issues is the increase in atmospheric carbon dioxide ($CO_2$) concentration as a result of its release from anthropogenic sources. $CO_2$ sequestration which includes capturing, separation and storage of carbon dioxide, targets a potential solution by mitigating the amount of $CO_2$ level in the atmosphere.

This work focuses on the last component of the aforementioned sequestration process: storage of $CO_2$. Coal seams, being attractive geological horizons, are chosen as potential repositories because there are several advantages where the sequestration costs can be offset in various ways.

The purpose of this research is to develop a tool for the practicing engineer, which predicts the important performance variables that are critical in $CO_2$ storage projects in coal seams. In this study, the neuro-simulation methodology, which basically couples the hard computing protocols with the soft computing protocols, is implemented. The PSUCOALCOMP, a compositional coalbed methane reservoir simulator, is used to generate the necessary training data sets used in the training of the artificial neural networks (ANNs) developed in this study.

The tested network predictions are found to be accurate. This observation indicates that most of the network predictions are sufficiently accurate to establish confidence in forecasting performances of coal sequestration processes without going through intensive numerical calculations. In other words, this work shows that with the use of the proposed tool a complex problem can be solved successfully.

## Appendix III.

## Abstract[3]

### "Regional Characterization of a Carbon Sequestration Pilot Site with Implications for Enhanced Oil Recovery"

**William Carpenter, West Virginia University**

The major goal of my thesis research is to develop a regional geological interpretation of a 9 township region surrounding the Stivason #4 $CO_2$ injection well at the DOE pilot site. Cross-sections, porosity distribution maps, and formation isopach and structure contour maps were constructed to identify major structures in the area that might serve as traps. Isopach maps were examined for influence of deeper structures reactivated during deposition. Late stage movement along deeper faults might produce subtle faulting and fracturing in shallower intervals that could promote $CO_2$ escape to the surface. The formations mapped in this study include not only the Permian Shattuck Sandstone Member, but also the encasing strata extending from the Devonian Woodford through the upper Permian Rustler formations.

The study also includes discussions of the physical characteristics of the overlying strata to help guide development of geomechanical models and flow simulations. These model studies and flow simulations will help evaluate the long-term integrity of the site in response to injection. The model studies and flow simulations also provide the framework in which to evaluate the long-term integrity of the injected $CO_2$.

The study also identifies additional structural traps that could be used for future sequestration activities. The regional characterization efforts undertaken here provide regional perspectives on the geologic integrity of reservoirs as well as their distribution and the potential volume of $CO_2$ that might be sequestered within the Shattuck Sandstone in this 400 square mile region.

The main objectives of this study are to provide detailed structure maps in the regional study area and to estimate the sequestration potential of the area. The success of carbon dioxide flooding from enhanced oil recovery in the area is discussed in the context of results from the pilot site. The presence of steep gradients in structural relief, areas of syndepositional thickening and thinning might reveal the presence of structures that could facilitate escape of $CO_2$ back into the Earth's atmosphere. The study will identify structural traps for sequestration in the region and provide an estimate of the total amount of $CO_2$ that could be sequestered into these reservoirs.

Following the regional assessment, a detailed evaluation of the West Pearl Queen pilot site geology is presented. As in the regional study, the main objective of the local study is to detail the structural history of the site. This involves detailed scrutiny of the structure and isopach maps as well as an estimation of physical properties such as density, Young's Modulus and Poisson's Ratio to aid in future studies. The structural analysis will help identify areas of differential movement through time, potential fault zones that may jeopardize the integrity of the sequestration seal at the pilot site. The study will also help locate appropriate monitoring technologies including water wells and capillary absorption tube samplers.

## Appendix IV.

## Abstract[4]

### "Fraction Pattern Characterization of the Tensleep Formation, Teapot Dome, Wyoming"

**Bryan Schwartz , West Virginia University**

This study presents a detailed analysis of open fracture systems observed in FMI logs through the oil producing Tensleep Formation at Teapot Dome. Open fracture systems in the Tensleep were compared to surface fracture distributions reported by Cooper (2000). Systematic fracture sets observed in the Tensleep consisted primarily of W and WNW striking sets oriented obliquely to the northwest trending hinge of the Dome and dipping on average between 78° and 58°. Hinge-parallel and hinge perpendicular sets, common at the surface, were rarely encountered in the wellbore. Observations were made in vertical wells along the hinge of the anticline where bedding is nearly horizontal, and the probability of intersecting vertical fractures, small. The present day maximum compressive stress inferred from drilling induced fractures is oriented, on average, N80W. $CO_2$ flooding and hydraulic fracturing will generally enhance production along the W and WNW open fracture trends.

2D fracture networks were created of the Tensleep Formation using the NETL program FRACGEN. Fracture orientation, dip and aperture measurements were calculated directly from FMI logs. Fracture dip, bedding plane dip, and the frequency of fractures per foot of borehole were used to determine fracture spacing. Fracture spacing appeared to increase in a broad linear fashion as the thickness of the Sandstone A and Sandstone B increased. The Dolomite B layer revealed a broad linear decrease per bed thickness. A histogram of fracture apertures indicated an exponential decay distribution. There are many small apertures (less than 0.0012in) and few large apertures (greater than 0.0028 in). A power law relationship between aperture and length was used to estimate fracture length in the Tensleep. Fracture lengths estimates range from 0.47 meters to 27.42 meters. Fracture lengths were shorter for the Sandstone A and Dolomite B layers, and larger for the thicker Sandstone B layer.

## Appendix V.

## Abstract[5]

### "Molecular Simulation of Study of Adsorption, Diffusion and Dissociation"

**Liang Chen, University of Pittsburgh**

There are two main objectives in my research work. The first objective is to investigate the adsorption behavior of various gases on single walled carbon nanotubes. This is accomplished by using the classical molecular simulation methods. Our simulation work has provided molecular level interpretation of some interesting phenomena observed experimentally by our collaborators. The second objective is to study the catalytic properties of metal/metal carbide surfaces and interfacial phenomena by using *ab initio* density functional theory.

We have studied the adsorption of various gases on carbon nanotubes by using classical molecular simulation and optimization techniques. We specifically have investigated the displacement of adsorption on di®erent adsorption sites. The systems investigated include $CO_2$ on SWNT, $Xe/CF_4$ on SWNT and $CO_2$/Xe on SWNT. Our simulations indicate that $CO_2$ is easily replaced from the endohedral and interstitial sites of SWNT bundles by Xe, while the groove/external surface sites loose much less $CO_2$. These calculations agree very well with the experimental observations. We have also observed unique one dimensional behavior of gases adsorbed on carbon nanotubes by using optimization and parallel tempering Monte Carlo. The results show that $CO_2$ molecules adsorbed in the groove sites of single walled carbon nanotubes display behavior that is quasi-1-dimensional. At finite coverages of $CO_2$ in grooves clusters containing only odd numbers of molecules are formed at low temperatures. Even numbers of molecules form two clusters, each containing an odd number of molecules.

## Appendix VI.

## Abstract[6]

### "Phase Equilibrium and Mass Transfer in Hydrate Forming $CO_2$-Water Systems"

**Yi Zhang, University of Pittsburgh**

Understanding the behavior and fate of $CO_2$ in aqueous systems is important both for developing potential $CO_2$ sequestration options and for understanding the impacts of seepage or leakage of the stored $CO_2$ into aqueous environments.

Two-phase equilibrium between $CO_2$ hydrate (H) and a water-rich liquid (L) are experimentally measured and theoretically described between 273 K and 280 K and at pressures up to 30 MPa. Concentrations of $CO_2$ in the water phase ranging between 0.0163 and 0.0242 mole fractions were studied. The theoretical and experimental results indicate that the equilibrium pressure is very sensitive to concentration at all temperatures. These equilibria represent the solubility of $CO_2$ hydrate in a water phase. The effect of salinity on the hydrate formation was also studied. A modified model which was based upon the variable chemical potential model of Lee and Holder (Lee and Holder, 2002) was introduced. There was a good agreement between the calculated and the experimental results, which further verified the theory. A simplified version of the model was also proposed that can provide quick and reasonable estimations of the equilibrium conditions of hydrates at low concentrations and medium to low pressures.

For the first time, the effect of thermal expansion of the occupied hydrate lattice is incorporated into the model. Accurate prediction of hydrate equilibria for several gases (methane, carbon dioxide and xenon) was obtained.

The third part of this work modeled dissolution rates of $CO_2$ droplets have been obtained under a range of conditions that include those that exist in the deep ocean down to 3000 m. A model was developed based on the dissolution rates obtained at different background concentrations of $CO_2$ that allows calculation of mass transfer coefficients at different temperatures and pressures. The impact of different background concentrations on the mass transfer coefficient was also investigated. The model also accounts for the impact of a hydrate coating on the drop. Utilization of our data for modeling may be desired to predict the fate of $CO_2$ released into aqueous environments like the deep ocean, since they were obtained under more realistic conditions.

## Appendix VII.

## Abstract[7]

### "Transient and Isotopic Infrared Study of Adsorbed Species on Heterogeneous Catalysts"

**Robert Stevens, Jr., University of Akron**

Heterogeneous catalysis involves adsorption, surface reaction, and desorption. Understanding the reaction mechanism can lead to design of more effective catalyst systems. Elucidation of the reaction mechanism requires determination of the structure of the surface intermediates and their behavior under different conditions (temperature, feed composition, etc.). We have utilized a technique that couples in situ infrared (IR) spectroscopy with mass spectrometry (MS) in the study of redox and acid-base type reactions. This technique allows the surface of the catalyst to be studied under reaction conditions, which generally leads to a unique perspective. We have chosen $CO_2$ reforming of $CH_4$ as a model reaction of the redox type due to its importance in production of synthesis gas. Pyridine adsorption onto sulfated zirconia was chosen as a model acid-base reaction due to its unique acid properties.

The $CO_2$ -$CH_4$ reaction over $Rh/Al_2O_3$ and $Rh/CeO_2$ was studied with pulse and step transient techniques. Linear CO was found to be the major species on $Rh/Al_2O_3$ during the reaction by IR; its accumulation on $Rh^0$ sites revealed that the surface of Rh crystallites on $Al_2O_3$ remained in a reduced state throughout the study. Steady-state isotopic transient studies at 773 K and 0.1 MPa showed that the formation of gaseous $^{13}CO$ closely followed that of adsorbed $^{13}CO$, indicating that linear CO is an active adsorbate. Pulsing $CH_4$ into $CO_2$ flow showed that the formation of $H_2$ led that of CO, revealing that the first step of the reaction sequence is the decomposition of $CH_4$ into $*CH_x$ species and hydrogen. Hydrogen activated $CO_2$ to produce linear CO. $O_2$ pulsing into $CO_2/CH_4$ over $Rh/Al_2O_3$ resulted in: (i) total oxidation of $CH_4$ to $CO_2$ and $H_2O$ and then (ii) a net increase in the formation of the desired products, $CO/H_2$, at a ratio of 1:1, revealing promotion of the $CO_2$-$CH_4$ reaction. $O_2$ pulsing into $CO_2/CH_4$ flow over $Rh/CeO_2$ led to only total oxidation, revealing that the catalyst is inactive for partial oxidation. A reaction mechanism is proposed and discussed.

The dynamic behavior of adsorbed pyridine and its interaction with the surface of sulfated zirconia and Pt-sulfated zirconia was elucidated by IR/MS. IR analysis confirmed that pretreating SZ in flowing He led to the formation of S=O species. Pyridine adsorption caused desorption of sulfur in the form of $SO_3$. IR and MS analyses coupled with a temperature-programmed desorption (TPD) study confirmed that pyridine adsorbed on the Lewis acid sites was oxidized to $CO_2$ while the pyridine-Brønsted acid site complexes showed little desorption or oxidation. Addition of Pt onto sulfated zirconia led to enhanced Brønsted acidity when treated with $H_2$ ; higher loading of Pt led to decreased thermal stability of the sulfate group, promoting desorption of $SO_2$ during the TPD.

## Appendix VIII.

## Abstract[8]

### "Fundamentals of Multiphase, Gas-Solid and Gas-Liquid Flows in Porous Media"

**Ali Reza Mazaheri, Clarkson University**

This thesis is concerned with fundamentals and applications of multiphase and particulate flows. The study contains three parts covering gas-liquid flows through porous media, gas-solid flows and Chemical-Mechanical Polishing (CMP).

A continuum model for multiphase fluid flows through poro-elastic media is developed. It is shown that the present theory leads to the extended Darcy's law and contains, as its special case, Biot's theory of saturated poro-elastic media. The capillary pressure formulation derived from the new model is used and the equation governing the evolution of the saturation and its temporal variation in porous media is derived. The resulting nonlinear diffusion equation is then solved numerically. The results show that the capillary hysteresis occurs when the temporal variation of saturation is included. Application of the developed model to $CO_2$ sequestration is discussed.

Computer simulations of dilute Gas-Solid flows in complex geometry regions are studied. A procedure for handling particle trajectory analysis in unstructured grid is developed. Examples of particle transport and removal in human lung and hot-gas cleaning systems are presented. The simulation results for the human lung show that the capture efficiency is affected by the turbulence in the upper three bifurcation airways. Computer simulations of gas-solid flows in hot-gas cleaning for a demonstration scale filtration system is studied in details. Alternative designs of the filter vessel are proposed. The corresponding vessel performance are numerically simulated.

Chemical mechanical polishing (CMP) has become critical to the fabrication of advanced multilevel integrated circuit in microelectronic industry. The effect of course surface roughness of abrasive particles on the polishing rate in CMP is studied. The effects of slurry pH and double layer attraction and repulsion on chemical-mechanical polishing are also studied. It is shown that the slurry pH and colloidal forces significantly affect the removal rate in chemical mechanical polishing.

## Appendix IX.

## Abstract[9]

### "Fundamentals and Applications of Environmental and Geophysical Multiphase Flows"

**Kambiz Nazridoust, Clarkson University**

This thesis is concerned with fundamentals and applications of environmental multiphase flows. The study contains four parts covering gas hydrate dissociation in porous media and rock fracture, gas-liquid flows in rock fractures, and transport of pollutants in outdoor air.

Dissociation of gas hydrate in a porous sandstone core as well as a fracture rock was studied using a computer modeling approach. Using Fluent™ code, an axisymmetric model of the core and a two dimensional model of the fracture were developed and solved for multiphase flows during the hydrate dissociation. The developed models account for the presence of three separate phases, namely, methane hydrate, methane gas, and liquid water. At the start of simulation, one end of the core/fracture was opened, exposing the hydrate to pressure below the hydrate equilibrium pressure; hydrate began to dissociate and methane gas and water began to flow. The depressurization was controlled by adjusting the pressure at the outlet valve of the core and/or fracture exit pressure. A comprehensive User Defined Function (UDF) for analysis of hydrate dissociation process was developed and implemented into the FLUENT code. The kinetic model introduced by Kim et al. (1986) was used in the new UDF, and could model multiple zones dissociation and multiphase flows. Variations of relative permeability of each phase were accounted for using Corey's model. The new computational model allowed for variations of the porosity with hydrate saturation. For different temperatures and various outlet pressures, the spatial and temporal variations of temperature, pressure and flow fields in the core/fracture were simulated. The time evolutions of methane gas and water flow rate were also evaluated. It was shown that the rate of hydrate dissociation was a function of surrounding environment temperature, outlet pressure condition, and sample permeability.

Single-phase fluid flows through a rock fracture were simulated. The fracture geometry was obtained from the CAT (Computerized Axial Tomography) scans of a rock fracture produced by the Brazilian method in a sandstone sample. A post-processing code using a CAD package was developed and used to generate the three-dimensional fracture from the CT scan data. Several sections along the fracture were considered and the Gambit™ code was used ot generate unstructured grids for flow simulations. FLUENT™ was used to analyze the flow conditions through the fracture section for different flow rates. It was confirmed that the pressure drop was dominated by the smallest aperture passages of the fracture. The accuracy of parallel plate models for estimating the pressure drops through fractures was studied. It was shown that the parallel plate flow model with the use of an appropriate effective fracture aperture and inclusion of the tortuosity factor could provide reasonable estimates for pressure drops in the fracture. On the basis of the CFD simulation data, a new expression for the friction factor for flows through fractures was developed. The new model predictions were compared with the simulation results and favorable agreement was found. It was shown that when the length of the fracture and the mean and standard deviation of the fracture are known, the pressure loss as a function of the flow rate could be estimated. These findings may prove useful for design of lab experiments, computational studied of flows through real rock fractures, or inclusions in simulators for large-scale flows in highly fractured reservoirs.

Dispersion of gaseous and particulate exhaust emissions in different street canyons was also studied. For two-dimensional sections of canyon models airflow, pollutant dispersion and deposition patterns in the streets and on the surrounding buildings were analyzed. Effects of building size, street width, and wind velocity on the pollutant transport were examined. While the stress transport turbulence models were used in most of the analysis, the predictions of other turbulence models were also examined. Depending on wind speed, building height, and street width, it was found that large recirculation regions in canyons may form. Under certain conditions, also pollutants emitted from vehicle exhaust may trap inside the street canyon. Variations of transport and deposition of emitted particulate pollutants with particle size and relaxation time were also studied. It was shown that the amount of deposited particles in street canyons reduces when the wind speed increases. The simulation results were compared with the available wind tunnel experiments and favorable agreement was found. In addition, a three dimensional simulation of the wind tunnel model was carried out using Large Eddy Simulation and was compared to the data and the previous findings.

The thesis was concluded with a listing of the future work and challenges that need to over come to complete the thesis.

## Appendix X.

## Abstract[10]

**"Simulation of Granular and Gas-Solid Flows using Discrete Element Method"**
**Dhanunjay Boyalakuntla, Carnegie Mellon University**

In recent years there has been increased research activity in the experimental and numerical study of gas-solid flows. Flows of this type have numerous applications in the energy, pharmaceuticals, and chemicals process industries. Typical applications include pulverized coal combustion, flow and heat transfer in bubbling and circulating fluidized beds, hopper and chute flows, pneumatic transport of pharmaceutical powders and pellets, and many more. The present work addresses the study of gas-solid flows using computational fluid dynamics (CFD) techniques and discrete element simulation methods (DES) combined. Many previous studies of coupled gas-solid flows have been performed assuming the solid phase as a continuum with averaged properties and treating the gas-solid flow as constituting of interpenetrating continua. Instead, in the present work, the gas phase flow is simulated using continuum theory and the solid phase flow is simulated using DES. DES treats each solid particle individually, thus accounting for its dynamics due to particle-particle interactions, particle-wall interactions as well as fluid drag and buoyancy. The present work involves developing efficient DES methods for dense granular flow and coupling this simulation to continuum simulations of the gas phase flow.

In this thesis, existing models (viz. the hard sphere and soft sphere models) for DES for spherical particles have been explored and the soft sphere model has been implemented. Efficient search algorithms and data structures for computing inter-particle interaction have been explored. Two different search algorithms, No-binary Search(NBS), and Quadtree/Octree search, have been implemented. The former provides an O(N) search procedure for like-sized particles. The latter is an O(NlogN) procedure, but can admit particles of different sizes.

Coupling of DES for solids and continuum for gas/liquid flow has also been done. The fluid flow computation has been done using MFIX, a solver developed at the Department of Energy's National Energy Technology Laboratory (NETL) for multiphase flows; the DES simulation provides the particle dynamics. In order to complete the coupled calculations, the void fraction and the volume averaged cell solid volume velocity corresponding to the DES particle distribution are computed. Interphase drag is computed from experimental correlations. Pressure force on the solids is also computed. Finally, a segregated coupling algorithm for the fluid and solid is used, with several DES time steps constituting one fluid time step. Granular temperature calculations are also done.

The DES-MFIX coupled code developed has been used to address two areas of industrial importance (i) granular material behavior with no fluid interaction (ii) gas-solid flows. For granular material behavior vibrated granular beds have been studied. For gas-solid flows, fluidized beds, which are of great importance in chemical engineering have been studied.

Simulations have been performed to observe pure granular behavior in vibrating beds. Benchmark cases have been simulated and the results obtained match the published literature. The dimensionless acceleration amplitude and the bed height are the parameters governing bed behavior. Various interesting behaviors such as heaping, round and cusp surface standing waves,

as well as kinks, have been observed for different values of the acceleration amplitude for a given bed height. Furthermore, binary granular mixtures (granular mixtures with two particle sizes) in a vibrated bed have also been studied.

Gas-solid flow simulations have been performed to study fluidized beds. Benchmark 2D fluidized bed simulations have been performed and the results have been shown to satisfactorily compare with those published in the literature. A comprehensive study of the effect of drag correlations on the simulation of fluidized beds has been performed. It has been found that nearly all the drag correlations studied make similar predictions of global quantities such as the time-dependent pressure drop, bubbling frequency and growth.

In conclusion, discrete element simulation has been successfully coupled to continuum gas-phase. Though all the results presented in the thesis are two-dimensional, the present implementation is completely three dimensional and can be used to study 3D fluidized beds to aid in better design and understanding. Other industrially important phenomena like particle coating, coal gasification etc., and applications in emerging areas such as nano-particle/fluid mixtures can also be studied through this type of simulation.

## Appendix XI.

## Abstract[11]

### "Predicting Gas Separation Membrane Performance from Atomistic Simulations"
### Shong-Shan Chong, Carnegie Mellon University

Gas separation using nanoporous membranes is a huge industry. In general computational methods are superior to experimental methods in guiding the design of reactors and to screen for the right materials to use in any particular gas separation application, in this thesis, we describe a method due to Skoulidas, Sholl and Krishna (SSK) for predicting the performance of nanoporous membranes from atomistic principles. Using detailed knowledge about the atomistic interactions between generally non-spherical alkanes in silicalite, we measure the adsorption isotherms followed by self, corrected and transport diffusivities self-consistently. For ethane, we show that these results compare very well with existing experiments using QENS and SCM. For the binary alkane mixtures of methane-ethane, methane-propane, ethane-propane, we combine the adsorption isotherms with the concentration diffusion coefficients of the single-component species to produce selectivity and flux predictions of the resulting binary gas mixture diffusing in a membrane of silicalite. We show that in general, selectivity increases when the feed pressure increases, favoring the lighter species. Finally, we apply the methods we have used to predict the selectivity of methane over carbon dioxide in MOF-5, a new class of nanoporous materials that may serve as good membranes. When the pressure drop is increased at fixed composition and feed pressure, the selectivities for carbon dioxide over methane increases dramatically. These results represent the first application of this method to elucidate the diffusion of nonspherical molecules in these class of materials.

## Appendix XII.

## Abstract[12]

### "Design and Study of Catalytic Activators of Hydrogen Peroxide Promising Rapid, Efficient Petroleum Desulfurization and Bleaching Technologies"

**Yelda Hangun-Balkir, Carnegie Mellon University**

The principles of green chemistry and the importance of replacing polluting oxidation technologies are introduced. A review of some recent inorganic catalytic systems that catalyze oxidations with hydrogen peroxide is presented. The systems that have potential for use in commercial oxidation technologies and industrial chemical synthesis are highlighted. Some applications that utilize hydrogen peroxide as an oxidant are discussed.

A new generation of oxidatively robust tetraamido macrocyclic ligands was synthesized. An iterative design process was employed, in which oxidatively sensitive ligand moieties were identified and replaced. One of the new ligands were prepared by a two step synthetic procedure previously used in the Collins group. A new synthesis was ultimately developed for the new ligand generation that provided significantly higher yields. Moreover, this new synthesis is more green since it has replaced the use of more toxic solvents.

The Fe(III)-$H_2O$ complex of each ligand in the new generation was synthesized and characterized to provide a pure Fe(III)-tetraamido complex with a labile axial ligand. The Fe(III)-$H_2O$ complexes were characterized by combustion elemental analysis along with UV/visible, IR, and ESI-MS spectroscopies.

The new Fe(III)-$H_2O$ complexes, resulting from a subtle change in ligand design feature, have significantly increased lifetimes that are sufficient to usefully activate $H_2O_2$ for oxidation in water from neutral to basic pH. The increased longevity of these complexes in activating $H_2O_2$ has been demonstrated by their ability, at nanomolar concentrations, to oxidize various dyes in water. Pinacyanol chloride was the analytically pure dye that were particularly used to establish this increased lifetime. UV/visible spectroscopy was used to measure dye bleaching times, to monitor the disappearance of dye absorbance, and to measure the amount of dye that was bleached before the complex degraded. The new Fe(III)-$H_2O$ complexes also have applications as catalytic $H_2O_2$ activators for green oxidation technologies. They activate $H_2O_2$ , at relatively low temperatures, for the selective and efficient oxidation.

Fe-TAML activator/hydrogen peroxide systems are used to bleach dyes in order to explore structure-reactivity relationship. The initial rates of dye bleaching by hydrogen peroxide were measured and compared by differently substituted Fe-TAML activators. Initial rates of dye bleaching were measured by UV/visible spectroscopy. The substituent effect on the catalytic activity was discussed.

U.S. EPA has mandated reduction of the maximum sulfur content in diesel to 15 ppm by 2006 and in gasoline to 30 ppm by 2004. The conventional method for reducing sulfur is hydrodesulfurization (HDS) under severe conditions. In order to reduce sulfur concentration in fuels, desulfurization of dibenzothiophene, 4-Methyl dibenzothiophene and 4,6-Dimethyl dibenzothiophene is required. Desulfruization of those compounds is very difficult by HDS due

to their steric-hindrance. Micromolar concentrations of Fe-TAML activators reacting with hydrogen peroxide convert greater than 99% of dibenzothiophene derivatives to the corresponding sulfones under mild conditions. The identification of the products was performed by combustion elemental analysis along with UV/visible, IR, GC-MS, NMR and GC-AED spectroscopies. The initial rates of the oxidation reactions were measured by UV/visible spectroscopy.

## Appendix XIII.

## Abstract[13]

### "First Principles Prediction of Hydrogen Transport in Binary Copper-Palladium Alloy Membranes"

**Preeti Kamakoti, Carnegie Mellon University**

Metal membranes play a vital role in hydrogen purification. Defect-free membranes can exhibit effectively infinite selectivity for hydrogen. Membranes must meet multiple objectives, including providing high fluxes, resistance to poisoning, long operational lifetimes, and low cost. Alloys offer an obvious route to improve upon membranes based on pure metals such as Pd. Development of new membranes is hampered by the large effort required to experimentally test membrane materials. We show how first principles calculations and coarse-grained modeling can accurately predict $H_2$ fluxes through binary alloy membranes as functions of alloy composition, temperature, and $H_2$ pressure. Our approach, which requires no experimental input apart from knowledge of bulk crystal structures, is demonstrated for PdCu alloys, which show nontrivial behavior due to the existence of fcc and bcc structures and have potential for resistance to sulfur poisoning. First, we used plane wave Density Functional Theory to study the binding and local motion of hydrogen for representative alloy compositions. This data was used to generate comprehensive models to predict hydrogen solubility and diffusivity in CuPd alloys over a wide range of compositions, temperatures and pressures. The accuracy of our approach is examined by a comparison with extensive experiments using thick PdCu foils at elevated temperatures performed by our coworkers at the National Energy Technology Laboratory. These experiments also demonstrate the ability of these membranes to resist poisoning by $H_2S$. We extend these methods to develop means to rapidly screen metal additives which when alloyed with CuPd would enhance the net hydrogen permeability. We performed in depth analysis of hydrogen solution and diffusion in CuPdRh alloys using methods analogous to those for binary CuPd alloys. Finally, ongoing work on CuPdRh and CuPdZn alloys is also discussed.

## Appendix XIV.

## Abstract[14]

### "Simulation of Dense Granular and Fluid-Solid Flow"
**Yong Cao, Carnegie Mellon University**

Flows of granular materials occur in a large variety of industrial applications, for example in fluidized beds, in the pneumatic transport of pellets, in pharmaceutical applications, in pulverized coal combustion, and many others. Granular flows of industrial interest occur in a variety of regimes. These include (i) the viscous or grain-inertia flow regime where momentary collisional contact dominates (ii) the elastic regime where granules are in constant frictional contact with each other, and (iii) the elastic regime where there is no motion. In most practical applications, all three regimes may exist at different points.

In recent years there has been a great deal of interest in developing computational models for fluid-solid flows to address a variety of applications in pneumatic transport, bubbling and circulating fluidized beds, and other areas. The most successful modeling has been in the viscous regime, and kinetic theories for granular flow have generally enjoyed success over the last two decades. On the other hand, both elastic and plastic regimes occur in many parts of the feed system such as in standpipes and L-valves. Recently, a variety of granular flow models addressing the elasto-plastic regime using hypoplasticity theory have begun to appear in the literature. A number of variants of hypoplasticity theory have been published. Their primary use thus far has been in the soil mechanics literature for describing the motion of sand. The theory relates the Jaumann stress tensor to a linear term proportional to the deformation tensor and a non-linear term proportional to the void ratio. Model constants for Karlsruhe sand have been published. The model includes history effects related to the instantaneous stress state, and an independence of the stress with respect to the shear rate.

The first objective of the present work is to develop a computational framework for the use of hypoplasticity theory to predict dense granular flow regimes for fluidized bed applications. The work focuses on the theory of Wu and Bauer and includes (i) development of a finite volume framework for the computation of hypoplastic stress tensor, and integration of this framework with a scheme for the computation of the solid flow and solid fraction field, (ii) implementation of the computational scheme in the MFIX software, (iii) application and testing of the theory and the developed numerical schemes for a range of operating conditions, and demonstration of its capabilities and limitations.

The case of flow during the filling of a rectangular domain is computed using the implementation. The findings to date indicate that the theory and the numerical scheme perform reasonably over a range of operating conditions. However, difficulties are encountered in the maximum packing limit. The hypoplasticity theory being considered allows the solid to pack beyond the maximum packing limit. Computations have been made employing modifications to the Wu and Bauer theory by employing additive terms to the stress tensor from plastic theory. This approach is shown to be successful in enforcing the maximum packing limit, but improvements are required to ensure robust numerical performance when the granular flow becomes fully packed.

Because of the limitations of hypoplasticity theory, a more reliable approach to computing dense granular and fluid-solid flows is necessary. The second objective of the thesis is to develop a discrete element simulation (DES) to simulating both dense granular flows and fluid-solid flows for general ellipsoidal particles. Nearly all published work in the DES area has assumed either spherical particles in 3D or circular discs in 2D. However, a variety of particles in industrial practice involve particulates of other shapes, particularly ellipsoids. These can be used to model flows of grains and beans, medical tablets and capsules, and with some modifications, in emerging applications such as nanotube/fluid mixtures. The present work involves developing efficient DES methods for ellipsoidal particles and coupling this simulation to continuum simulations of the fluid phase flow.

A soft sphere model for DES is extended for use with ellipsoidal particles. An elliptical particle overlap detection method is developed for use in contact force determination. An efficient quadtree/octree search algorithm is used for neighbor detection. Three-dimensional chute flow is computed and comparisons with previously published simulations and experiments are presented. The comparisons suggest the correct imposition of surface boundary conditions is critical in making accurate predictions. The model is also used to simulate pure granular flows in vibrating beds. Flow regime maps are developed and differences between the behavior of spherical and elliptical particles are presented. Finally, the discrete element simulation is coupled to a simulation of fluid flow using the MFIX code. Fluid-solid coupling is achieved through the use empirical correlations for non-spherical particles in packed beds. The model is used to compute fluid-solid flow in a driven cavity as a demonstration. The time required for fluidization is computed as a function of the lid Reynolds number are computed. These studies suggest that DES simulations are a powerful tool for exploring the behaviors of complex liquid solid mixtures of realistic industrial particulates.

## Appendix XV.

## Abstract[15]

### "Design and Understanding of Turbulent, Bubbling and Slurry Bubble Column Reactors"

**Jonghwun Jung, Illinois Institute of Technology**

Major oil companies are gearing up to build slurry bubble column reactors (SBCR) to utilize natural gas located in remote areas of the world and to convert it to paraffin wax which will be upgraded to gasoline and Diesel fuels. Computational fluid dynamics (CFD) is a recently developed tool which can help in the scale up. However, before such a tool becomes useful many theoretical questions must be answered. This thesis is an attempt to address some of the unresolved critical issues.

Formation of bubbles in fluidized beds is a critical issue that must be resolved before a reliable scale-up is possible. Two computer codes, the IIT code and the MFIX code, were used to compute bubbles in gas-solid fluidized beds. The experiments which were simulated were two dimensional bubbling beds at IIT with 530 micron glass beads. Measurements included the determination of bubble sizes, bubble velocities and two types of granular temperatures, one due to particle oscillations and second due to the motion of bubbles. The computed bubble sizes and shapes matched the observed sizes and shapes determined using a video camera. The use of higher order numerics produces better bubble resolution due to smaller numerical diffusion. The computed axial solids velocity, the granular temperature near the center of the bed, and the bubble rise velocity agree with measurements done using our CCD camera technique.

A criterion for bubble formation was found. For the bubble formation the inelastic particle dissipation must be greater than the ratio of the granular temperature to the square of the slip velocity. This means there will be no bubble formation for sufficiently elastic particles. The computed bubble size is a function of the restitution coefficient which is of the order of 0.99 for Geldart B particles.

No bubbles were observed in the experiments with 10 nm size particles. Fluidization and collapsing bed experiments were performed with "Tullanox", 10 nm diameter fumed silica. The minimum fluidization velocity was determined to be 0.0l15m/sec at the unusually low volume fraction of solids of 0.0077. The solids volume fraction was measured using a gamma-ray densitometer. Fluidization was without large bubbles, with a high bed expansion ratio. The sedimentation process was simulated using a two-fluid hydrodynamic model. The input into the model was a measured solids stress modulus and an agglomerate size determined from the settling curves. With these two rheological parameters, there was good agreement between the sedimentation theory and the experiment. This study shows that the standard collapse bed experiment used in industry is a good test of rheological properties of particles.

A critical issue in the SBCR which has not been addressed in the literature is that of optimum particle size. Optimum sizes were determined in two different ways. One optimum was found for maximum granular temperature. The size was 60 microns. The second optimum was determined for maximum methanol production in a SBCR. The optimum particle size was 70 microns.

## Appendix XVI.

## Abstract[16]

### "Characterization of Precipitates Associated with Bituminous Coal Mine Drainage, Northern Appalachian Region, United States"

**Candace Kairies, University of Pittsburgh**

Changes in precipitate mineralogy, morphology, and major and trace elemental concentrations and associations throughout five coal mine drainage remediation systems in Pennsylvania and Maryland that treat discharges of varying chemistries were investigated. The precipitates are dominantly (>70%) goethite with minor amounts of other iron and/or manganese oxides and quartz. Crystallinity varies throughout an individual system and is a function of the treatment system and how rapidly ferrous iron oxidizes, precipitates, and settles. Precipitates formed earlier in the systems have the highest crystallinity; less crystalline precipitates are associated with enhanced sorption of trace metals. High surface area and vacancies within the goethite structure enable incorporation of metals from mine drainage polluted waters. Sorption affinities follow the order Al>Zn>Co≈Ni>Mn. As pH increases in the individual treatment systems toward the pHpzc, arsenic sorption decreases and aluminum and transition metal sorption increases. Sulfate, sodium and ferrous iron potentially influence the sorption of trace metals.

A sequential extraction procedure was developed to determine how trace elements are associated with the precipitates. Arsenic, cobalt, manganese, nickel and zinc are not released until the iron hydroxide phase is dissolved, indicating these metals are either tightly sorbed to the surface or incorporated into the hydroxide structure. Cobalt and nickel preferentially partition into a manganese oxide/hydroxide phase (if present), over the iron hydroxide phase. The stability of the precipitate controls the long-term mobility of trace metals. Associated trace metals will remain unavailable to the environment as long as the precipitate is not altered.

Additionally, spatial and temporal variations between precipitates formed from a net-alkaline coal mine discharge were examined. The precipitates are all moderately crystalline goethite with minor variations in morphology and composition. They contain 20 – 30% more iron than the natural mined iron oxides examined in this study, and concentrations of manganese, nickel and zinc are up to three orders of magnitude lower than the natural iron oxides. Geochemical analysis indicates that mine drainage precipitates formed from net-alkaline waters are of a higher purity than natural iron oxides. Results of this study have implications for disposal, resource recovery, and the optimization of mine drainage passive remediation systems.

## Appendix XVII.

## Abstract[17]

### "Evaluation of the Kinetics of Biologically Catalyzed Treatment and Regeneration of Nitrogen Oxide Scrubbing Process Waters"

**Robert Dilmore, University of Pittsburgh**

A prototype apparatus was configured and operated to evaluate the efficacy of a process that integrates the absorption of nitric oxide in an aqueous solution of ferrous ethylenediamintetraacetic acid (Fe(II)EDTA) with biological treatment and regeneration of spent scrubber water. In addition to operation of a continuous-flow, closed-loop prototype process, a series of batch reactor tests were conducted to investigate the kinetics of microbially-catalyzed reduction of the nitrosyl adduct of ferrous EDTA and microbially-catalyzed reduction of oxidized ferric EDTA. Denitrifying and strictly anaerobic biomass from a municipal wastewater treatment process was cultivated using ethanol as the primary electron donor and nitrate and ferric EDTA as electron acceptors. Following 42-days of bioreactor startup, nitric oxide (NO) scrubbed from a counter-current absorption tower replaced nitrate. After 27 days of acclimation, an 80-day period of steady state operation was observed. During steady state operation, mean NO scrubbing efficiency of 97.9% was achieved, process water oxidation/reduction potential (ORP) remained between -75 and -140 mV (vs. Ag/AgCl ref.), and generated biogas was 91% N2, by volume. Biomass in the prototype reactor was flocculent, and traveled throughout the closed-loop process. Because of the constant recirculation of washed-out biomass and low observed biomass yield (0.0393 g VSS/g COD), mass balance showed the prototype process sludge age to be 75.9 days. During steady state operation, biomass was extracted for kinetic batch analyses. Batch reactor kinetic tests revealed that both ferric EDTA and NO reduction proceed as a result of microbially-catalyzed reactions. Microbially-catalyzed reduction of ferric EDTA proceeds according to the Monod kinetic model, while strong inhibition of the microbially-catalyzed reduction of NO·Fe(II)EDTA was observed at ethanol concentrations above 0.33 g COD/l. Based on observed population parameters, including biomass yield, endogenous decay, and substrate utilization rate, the critical mean cell retention time below which wash out of a continuously-stirred bioreactor would occur was found to be 11.7 days and 51.4 days for NO reducers and ferric EDTA reducers, respectively. Experimental results provide insight into conditions required for the successful operation of a process for the biological treatment and regeneration of spent scrubber solution from a NOX absorption process.

## Appendix XVIII.

## Abstract[18]

### "The High-Temperature, High-Pressure Homogeneous Water-Gas Shift Reaction in a Membrane Reactor"

**Filipe Bustamante, University of Pittsburgh**

The transition to a hydrogen economy requires substantial reductions in the cost of hydrogen. One alternative for achieving this goal is to conduct the water-gas shift reaction under the high temperature and pressure conditions present at the coal gasifier outlet. However, the equilibrium conversion of the water-gas shift reaction at such high temperatures is quite low. Even though the thermodynamic limitation can be overcome by the introduction of a $H_2$-selective membrane reactor, no previous studies of such a membrane reactor concept have been performed. The objective of this work is to provide the fundamental background required to determine whether the high-temperature, high-pressure water-gas shift reaction in a $H_2$-selective membrane reactor, despite its theoretical simplicity and potential advantages, is a viable way to enhance the hydrogen yield.

The gas-phase reaction kinetics were studied in the presence of an inert material (quartz), a common high-temperature construction material (Inconel®600) and potential membrane materials (Pd and a Pd-Cu alloy) in an effort to assess if the reaction can proceed at rates high enough to preclude the need for added catalysts. The gas-phase mechanism previously proposed to describe the high-temperature, low-pressure reaction was found to be valid at high-pressure conditions. Inconel®600 surfaces greatly enhanced the reaction rate. This effect is likely attributable to the formation of a catalytic chromium oxide layer on the metal surface. Fresh Pd-Cu pellets and, also, Pd and Pd-Cu surfaces after exposure to reaction conditions followed by an oxygen treatment for carbon removal displayed catalytic activity for the water-gas shift reaction. However, the catalytic effect was not as significant as that observed with Inconel®600 surfaces. These results suggest that sufficiently large reaction rates can be attained without the need of an external catalyst.

Several Pd-based membrane reactor configurations were studied. The reaction was conducted in high-reaction rate / low-permeation rate (flat disk) and high-permeation rate / lowreaction rate (tubular) membrane reactor configurations. Conversions surpassing the equilibrium limitation were attained with both configurations. The two approaches are compared. It was found that the heat released by the reaction in the tubular configuration may have a significant, enhancing effect on the reaction conversions.

## Appendix IXX.

## Abstract[19]

### "Environmentally Relevant Adsorption on Carbonaceous Surfaces Studied by Optical Differential Reflectance and Temperature Programmed Desorption"

**Seokjoon Kwon, University of Pittsburgh**

This study evaluated the application of a versatile optical technique to study the adsorption and desorption of model adsorbates representative of volatile polar (acetone) and non-polar (propane) organic compounds on a model carbonaceous surface under ultra high vacuum (UHV) conditions. The results showed the strong correlation between optical differential reflectance (ODR) and adsorbate coverage determined by temperature programmed desorption (TPD). The ODR technique was found to be a powerful tool to investigate surface adsorption and desorption from UHV to high pressure conditions.

The effects of chemical functionality and surface morphology on the adsorption/desorption behavior of acetone, propane and mercury were investigated for two model carbonaceous surfaces, namely air-cleaved highly oriented pyrolytic graphite (HOPG) and plasma-oxidized HOPG. Oxygen-containing functional groups exist on both air-cleaved and plasma-oxidized HOPG. They can be removed by thermal treatment (>500 K). The presence of these groups almost completely suppresses propane adsorption at 90 K and removal of these groups leads to a dramatic increase in adsorption capacity. The amount of acetone adsorbed is independent of surface heat treatment and depends only on total exposure. The effect of morphological heterogeneity is evident for plasma-oxidized HOPG as this substrate provides greater surface area, as well as higher energy binding sites. Mercury adsorption at 100 K on HOPG surfaces with and without chemical functionalities and topological heterogeneity created by plasma oxidation occurs through physisorption. The removal of chemical functionalities from HOPG surface enhances mercury physisorption. Plasma oxidation of HOPG provides additional surface area for mercury adsorption. Mercury adsorption by activated carbon at atmospheric pressure occurs through two distinct mechanisms, physisorption below 348 K and chemisorption above 348 K. No significant impact of oxygen functionalities was observed in the chemisorption region.

The key findings of this study open the possibility to apply scientific information obtained from studies with simple surfaces like HOPG under ideal conditions (UHV) to industrial sorbents under realistic process conditions. HOPG surfaces can be modified chemically and topologically by plasma oxidation to simulate key features of activated carbon adsorbents.

## Appendix XX.

## Abstract[20]

### "Chemistry of the Adsorption of Carbon Dioxide by Argonne Premium Coals and a Model to Simulate Carbon Dioxide Sequestration in Coal Seams"

**Ekrem Ozdemir, University of Pittsburgh**

The interactions of $CO_2$ with coal were investigated under a set of conditions to determine the effects of the nature of the coal and the sequestration environment including parameters such as rank and moisture content of the coal, the temperature, pressure, and pH. A mathematical model was also developed to simulate the coal bed methane production and the $CO_2$ sequestration processes.

The excess adsorption and desorption isotherms of $CO_2$ on eight Argonne Premium coal samples were measured using the volumetric method. The isotherms were found to be rectilinear and fit to the conventional adsorption model equations poorly due to the coal swelling. An adsorption isotherm equation was derived to account for the volumetric changes and significantly better fits were obtained. Upon drying, the volume of coals was determined to shrink, which was about 2% to 5% for medium and high rank coals, and up to 40% for the low rank coals. The swelling of coals during adsorption isotherm measurements in $CO_2$ was estimated to be about the same as the shrinkage that occurred during the moisture loss. If the swelling was not included in the adsorption isotherm equation, the reported adsorption capacities and surface areas of the coals were overestimated by about 15%. The adsorption capacities of moisture-free Argonne coals were found to be about 2.2 ± 0.8 mmole/g-coal, daf basis and to be lower in wet coals. The isosteric heat of adsorption for $CO_2$ on Argonne coals was estimated to be about 25±2 kJ/mole, regardless of the coal rank. The adsorption capacity of $CO_2$ on the weak solutions of acid leached coals was higher than both the base leached and untreated coals, possibly due to the removal of ash content of the coals.

The modeling results developed to simulate the $CO_2$ injection process suggest that the $CO_2$ can be injected at a rate of about 10*103 standard $m^3$ per day. The injected $CO_2$ will reach the production well, which is separated from the injection well by 826 m, in about 30 years. During this period, about 160*106 $Sm^3$ of $CO_2$ can be stored within a 2.14 $(km)^2$ coal seam.

## Appendix XXI.

## Abstract[21]

### "Simulations of Adsorptions and Phase Transitions"
### Wei Shi, University of Pittsburgh

The objective of this thesis is to develop simulation tools that will allow us to study many phenomena from a molecular level. The topics covered in this thesis include bulk phase transitions, phase transitions in adsorbed fluids, and the application of single-walled carbon nanotubes as a gas storage media.

Multiple histogram reweighting and mixed-field finite-size scaling techniques have been developed to calculate the phase diagram for classical and quantum fluids in bulk and adsorbed phases. We show, for the first time, that capillary condensation shows a crossover of the effective exponent for the width of the coexistence curve from 2-D Ising-like (1/8) farther away from the critical point to mean-field (1/2) near the critical point. The first prewetting transitions clearly observed from simulation of quantum fluids are presented. The experimental wetting temperature of 19.1 K is reproduced from the simulation with a modified potential. Hydrogen adsorbing on a 15 Å thick fillm of Rb on Au gives a wetting temperature of about 1 K less than $H_2$ on pure Rb. This prediction should be observable from experiments.

Hydrogen adsorption onto single walled carbon nanotube bundles has been performed from computer simulations and compared with the experiments. We study the effect of $CO_2$ oxidation of the nanotubes on adsorption. Isotherms computed with a standard graphitic potential give remarkably good agreement with the experimentally measured isotherms before activation with $CO_2$. The effect of activation is modeled by independently increasing the nanotube spacing and the solid-fluid interaction potential. It is found that only a combination of increased nanotube spacing and increased solid-fluid potential gives rough agreement with experiments.

Gases such as $CH_4$, Xe, and Ar have been studied on both the homogeneous (same tube diameter) and heterogeneous (different tube diameters) closed single-walled carbon nanotube bundles constructed from the basin-hopping method. Experimental gas adsorption data on SWNT bundles have previously been analyzed in terms of an over-simplified model of homogeneous nanotubes packed into perfect arrays. This analysis has led to the general conclusion that gases do not adsorb inside interstitial channels of homogeneous nanotube bundles. Our analysis overturns the current paradigm of gas adsorption on SWNTs by showing that adsorption inside interstices of heterogeneous SWNT bundles is vitally important to accurately describing these materials.

## Appendix XXII.

## Abstract[22]

**"A Dilatant Double Shearing Model for Granular Materials including the Effects of Fabric"**
**Huaning Zhu, Tulane University**

In the present study, we develop a dilatant double shearing model for granular materials incorporating the effects of fabric and its evolution in order to capture the inherent and induced anisotropic behavior and the complex cyclic shear loading response of granular materials. Unlike Anand and Gu's (2000) model where the two shearing rates are taken to be equal, we can have different shearing rates along the two slip systems by considering the fabric. This property leads to non-coaxiality of the principal axes of stress and strain rate, which is more appropriate for a material that exhibits initial and induced anisotropy. We also propose an evolution equation for the fabric tensor. In addition, we assume an orthotropic elasticity tensor with the axes of orthotropy coincident with the principal axes of the fabric tensor and the components of the elasticity tensor dependent on the invariants of the fabric tensor. The model developed in this paper also includes the experimentally observed characteristics of granular materials: the gradual concentration of the contact normals towards the maximum compressive principal stress direction. We then implement the constitutive equation of the model into ABAQUS/Explicit by writing a user material subroutine and use it to conduct the biaxial compression tests under different initial bedding angles and investigate the responses of this model under the cyclic shear loading conditions. The predictions of this model show good quantitative agreement with the experiments of Park (1990), Park and Tatsuoka (1994) and Okada (1992).

We then extend the plain strain dilatant double shearing model to three dimensions. We use this model to conduct the numerical triaxial compression tests for granular samples with different initial anisotropy and the numerical computations for the stress state in a static conical sand pile. The numerical results show that the extended constitutive model is able to capture the strength anisotropy behavior of granular materials.

We finally make a comparative study of the responses of the present model and the hypoplastic model. We find our newly developed model is easy to calibrate and gives close stress ratio and void ratio responses to the predictions of hypoplastic model under most conditions.

## Appendix XXIII.

## Abstract[23]

### "Experimental Investigation of Oscillatory Heat Release Mechanisms and Stability Margin Analysis in Lean-Premixed Combustion"

**Don Ferguson, West Virginia University**

Lean-premixed combustion has become an acceptable means of achieving ultra-low NOx emissions from land-based gas turbines. Further reduction may be possible through the use of hydrogen augmented or syngas fuels. However, advanced combustor designs developed to utilize these technologies often encounter thermoacoustic instabilities that may significantly hamper engine performance and shorten component life-cycles. These dynamics, although not fully understood, occur through a complex interaction between variations in heat release rate and acoustic properties of the system, and can be exacerbated by variable fuel properties in natural gas and syngas applications.

Theoretical models of thermoacoustic instabilities have attempted to describe the coupling process through reduced-order models that represent mechanisms suspected of contributing to variations in the heat release rate such as variations in fuel/air mixing, fluctuations of heat release through vortex shedding and periodic changes in the flame structure. These reduced-order models have demonstrated only a modest ability at predicting instabilities even in relatively simple systems. This may be due to the inherent complexity from interacting processes, the use of over-simplifying assumptions and the lack of experimental verification.

In this study a simple conical flame, used to reduce the number of contributing mechanisms, is utilized to experimentally evaluate the relationship between the heat release rate and variations in the flame surface area. Results indicated that while area perturbations can adequately describe the magnitude of heat release fluctuations, the area perturbations are not a direct indicator of the phase of heat release needed for closed-loop stability analysis.

Time-resolved particle image velocimetry was used to quantify the near-field acoustics and the dilatation rate field in the pre- and post-flame regions of the flow. Measurements indicated that multi-dimensional acoustics dominate the pre-combustion flow field with radial and axial acoustic velocities of similar magnitudes. Variations in the flame structure potentially due to alternating regions of positive and negative flame stretch were also observed and may result in variations in the flame speed. As it is common to assume constant flame speed and one-dimensional acoustics, the experimental identification of these altered mechanisms may help to resolve discrepancies compared to a number of published reduced-order models.

## Appendix XXIV.

## Abstract[24]

### "Geophysical investigation of the T and T Mine Complex, Preston County, West Virginia"

**Jennifer Mabie, West Virginia University**

The U.S. Department of Energy National Energy and Technology Laboratory have utilized an airborne platform with remote sensing technologies consisting of a multi-spectral scanner and airborne electromagnetic conductivity technologies to provide a rapid reconnaissance of watershed areas. Airborne surveys were flown over the T&T Mine Complex, located in Preston County, West Virginia. The electromagnetic and thermal anomalies observed in the airborne data were compared to mine maps to correlate anomalous features with mine pools and ground water discharge points that may represent acid mine drainage (AMD). Surface geophysical studies were performed to delineate the conductivity anomalies observed in the airborne data. The geophysical surveys were not able to resolve the mine pool at a depth of 90 meters; however, there was resolution between airborne and ground survey results up to a depth of 40 meters. The thermal data was not able to resolve groundwater discharge points that may represent AMD.